STUDY ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HIGH TEMPERATURE ELECTROSPUN POLYETHYLENE FIBERS

A Thesis
Presented to
The Graduate Faculty of The University of Akron

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

Qian Li
August, 2012
STUDY ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HIGH TEMPERATURE ELECTROSPUN POLYETHYLENE FIBERS

Qian Li

Thesis

Approved:                                      Accepted:

Advisor                                      Department Chair
Dr. Shing-Chung Wong                          Dr. Celal Batur

Committee Member                              Committee Member
Dr. Xiaosheng Gao                             Dr. Todd A. Blackledge

Dean of the College                           Dean of the Graduate School
Dr. George K. Haritos                         Dr. George R. Newkome

Date
ABSTRACT

It has been recognized for a long time that very strong and stiff materials can be prepared from polymers. Take polyethylene for example, the reported theoretical strength and modulus are 33 GPa and 440 GPa respectively if perfect extended polymer molecules are arranged parallel to fiber axis. Even such an idealized conformation cannot be obtained in practice; however gel-spun UHMWPE fibers, commercialized in the late 1970s, are characterized by a high Young’s modulus, up to 265 GPa and a high tensile strength, up to 7.2 GPa.

Electrospinning has evinced more interest recently due to its versatility and its ability to consistently produce fibers in the submicron range. However, electrospinning of polyethylene (PE) is challenging and only few reports have appeared on it up to date. It is because of its poor electrical conductivity and the lack of an appropriate solvent at room temperature. In the thesis, 15 wt. % -22 wt. % of linear low density polyethylene (LLDPE) is electrospun into fibers at high temperature. The fiber morphology, crystallinity, crystallite structure, thermal and tensile properties of electrospun fibers are evaluated as a function of concentration. It shows that the crystallinity increased from 28.7% to 50.4% by increasing the solution concentration from 15 wt. % to 22 wt. % And the increasing concentration and crystallinity result tensile modulus and strength enhancements of fibers. The mechanical properties of single fibers were also improved
when incorporating graphene into fibers. In addition, a size effect is observed from the tensile behavior of electrospun single fibers. A significant increase in modulus and strength of the fibers is demonstrated when the size of the fiber decreased below 1 µm. Thus, it is demonstrated submicron size polyethylene fibers with high strength can be achieved by electrospinning.
ACKNOWLEDGEMENTS

First and foremost, I would like to thank my advisor Dr. Shing-Chung Wong for all his guidance, support, and assistance to this project. I would like to thank my committee members, Dr. Xiaosheng Gao and Dr. Todd A. Blackledge for their time and advice.

I would like to thank the Department of Mechanical Engineering, Department of Biology, College of Polymer Science and Polymer Engineering at The University of Akron. I am truly thankful to Dr. Blackledge and his group for helping me on operation of Nano Bionix. I am deeply thankful to Dr. Reneker’s group for helping me with electrospinning. I am also genuinely thankful to Dr. Rong Bai for teaching me how to use the instruments of DSC, XRD.

Lastly, I would like to thank all my friends including each member of Dr. Wong’s group for their help and friendship.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>CHAPTER</td>
<td>1</td>
</tr>
<tr>
<td>I INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II LITERATURE REVIEW</td>
<td>3</td>
</tr>
<tr>
<td>2.1. The Essence of Polyethylene</td>
<td>3</td>
</tr>
<tr>
<td>2.1.1. Classification of Polyethylene</td>
<td>4</td>
</tr>
<tr>
<td>2.1.2. Crystal Morphology and Crystallization</td>
<td>7</td>
</tr>
<tr>
<td>2.1.2.1 Three-phase Morphology</td>
<td>7</td>
</tr>
<tr>
<td>2.1.2.2 Crystall Unit Cells</td>
<td>9</td>
</tr>
<tr>
<td>2.2. Graphene</td>
<td>13</td>
</tr>
<tr>
<td>2.2.1 Properties of Graphene</td>
<td>13</td>
</tr>
<tr>
<td>2.2.2 Graphene/Polymer Nanocomposites</td>
<td>14</td>
</tr>
<tr>
<td>2.2.3 Production of Graphene</td>
<td>15</td>
</tr>
<tr>
<td>2.3. Polymeric Nanofibers</td>
<td>17</td>
</tr>
<tr>
<td>2.3.1 Electrosprning Set Up and Process</td>
<td>17</td>
</tr>
<tr>
<td>2.3.2 Parameters of the Electrosprning Process</td>
<td>19</td>
</tr>
</tbody>
</table>
2.3.2.1 Solution Parameters .......................................................................................... 19
2.3.2.2 Electrospinning Process Parameters ............................................................. 22
2.3.3 Structural Properties of Electrospun Fibers ......................................................... 24
  2.3.3.1 Molecular Orientation .................................................................................... 25
  2.3.3.2 Crystallinity .................................................................................................... 25
  2.3.3.3 Effect of Fiber Diameter on the Structural Properties ..................................... 26
  2.3.3.4 Effect of Collector on Structural Properties ............................................... 26
2.3.4 Mechanical Properties of Electrospun Fibers ..................................................... 27
  2.3.4.1 Effect of Structural Morphology on Tensile Properties .............................. 27
  2.3.4.2 Effect of Collector Type on Tensile Properties .......................................... 28
2.3.5 History of Production of Polyethylene Fibers ...................................................... 29
2.3.6 Application of Electrospun Nanofibers ............................................................... 31
  2.3.6.1 Tissue Engineering Application ................................................................. 31
  2.3.6.2 Electrospun Fiber Reinforced Composites .................................................. 32
  2.3.6.3 Filtration ....................................................................................................... 32

III EXPERIMENTAL WORK ....................................................................................... 33

3.1 Material .................................................................................................................. 33

3.2 Production of Graphene by Exfoliation of Graphite .............................................. 33

3.3 Electrospinning Process ......................................................................................... 34
  3.3.1 Fabrication of Linear Low Density Polyethylene fibers ................................. 34
  3.3.2 Fabrication of LLDPE/Graphene Composit fibers ........................................ 36

3.4 Differential Scanning Calorimetry ....................................................................... 37
3.5 X-Ray Diffraction Analysis ................................................................. 38
3.6 SEM Analysis ......................................................................................... 40
3.7 Diameter Measurement ................................................................. 40
3.8 FTIR .................................................................................................. 41
3.9 Mechanical Testing ........................................................................... 42
   3.9.1 Sample Preparation and Tensile Test ....................................... 42

IV RESULTS AND DISCUSSION ................................................................. 44

4.1. SEM Analysis ................................................................................... 44
4.2. WAXD Analysis .............................................................................. 53
4.3. DSC Analysis .................................................................................. 60
4.4. FTIR Analysis ................................................................................ 65
4.5. Tensile Testing ............................................................................... 67
   4.5.1 Mechanical Properties of Electrospun LLDPE Fibers .............. 67
   4.5.2 Mechanical Properties of Electrospun LLDPE/Graphene Composite Fibers 72

X CONCLUSIONS ......................................................................................... 76

REFERENCES ......................................................................................... 77
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>X-ray diffraction analysis results</td>
</tr>
<tr>
<td>4.2</td>
<td>X-ray diffraction analysis results [120]</td>
</tr>
<tr>
<td>4.3</td>
<td>Thermal analysis results</td>
</tr>
<tr>
<td>4.4</td>
<td>Main absorption bands of polyethylene and their assignments</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>2.1</td>
<td>Chemical structure of pure polyethylene</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic representation of high density polyethylene</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic representation of low density polyethylene</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematic representation of linear low density polyethylene</td>
</tr>
<tr>
<td>2.5</td>
<td>Schematic representation of very low density polyethylene</td>
</tr>
<tr>
<td>2.6</td>
<td>Schematic representation of the three phases contained in solid polyethylene</td>
</tr>
<tr>
<td>2.7</td>
<td>Tie chains, loops, and cilia in the noncrystalline phases of polyethylene</td>
</tr>
<tr>
<td>2.8</td>
<td>Generic unit cell</td>
</tr>
<tr>
<td>2.9</td>
<td>Polyethylene orthorhombic unit cell (a) orthogonal view; (b) view along axis</td>
</tr>
<tr>
<td>2.10</td>
<td>Polyethylene monoclinic unit cell [22]</td>
</tr>
<tr>
<td>2.11</td>
<td>Polyethylene hexagonal unit cell [22]</td>
</tr>
<tr>
<td>2.12</td>
<td>Graphene structure of single two-dimensional hexagonal sheet of carbon atoms</td>
</tr>
<tr>
<td>2.13</td>
<td>Schematic of the general laboratory setup used for an electrospinning experiment (a) image of the Taylor cone and (b) image of the bending instabilities [72]</td>
</tr>
<tr>
<td>2.14</td>
<td>SEM images of electrospun nanofibers with beads from different polymer concentration solutions [73]</td>
</tr>
<tr>
<td>2.15</td>
<td>Schematic of the shape of pendent drop changed with increasing voltage</td>
</tr>
</tbody>
</table>
2.16 Structural morphology of electrospun fibers displaying the dense packed lamella and fabrilla. .......................................................... 26

2.17 SEM of HDPE fiber formed in an electrically driven jet of 1% polyethylene in paraffin [96]. ................................................................. 32

2.18 FESEM of LLDPE electrospun fiber at 3K and 15K magnification [99] ............. 32

2.19 Micrographs showing the surface of UHMWPE fiber electrospun from solutions in a 1:1 (w/w) mixture of p-xylene and CH at different UHMWPE concentrations: (a) 0.2, (b) 0.1 [100]S ......................................................... 33

3.1 Dispersion of graphene after sonication for 2 hours ........................................... 37

3.2 A schematic of the high temperature electrospinning setup. ......................... 38

3.3 Image of LLDPE/decalin/ graphene dispersion ............................................ 39

3.4 Digital picture of the TA instruments DSC .................................................. 40

3.5 Digital picture of the wide-angle X-ray diffraction instrument ..................... 42

3.6 Preparation of single electrospun fiber for tensile test ................................. 45

3.7 Instrument used for testing: MTS Nano Bionix® ........................................ 46

4.1 Plot of the variation of average fiber diameter vs. concentration ................. 48

4.2 SEM picture of e-spun LLDPE fiber with 15% concentration at magnification 1200 ................................................................. 49

4.3 SEM picture of e-spun LLDPE fiber with 15% concentration at magnification 2000 ................................................................. 49

4.4 SEM picture of e-spun LLDPE fiber with 18% concentration at magnification 1200 ................................................................. 50

4.5 SEM picture of e-spun LLDPE fiber with 18% concentration at magnification 2000 ................................................................. 50

4.6 SEM picture of e-spun LLDPE fiber with 20% concentration at magnification 1200 ................................................................. 51
4.7 SEM picture of e-spun LLDPE fiber with 20% concentration at magnification 2000 .................................................................................................................... 51

4.8 SEM picture of e-spun LLDPE fiber with 22% concentration at magnification 1200 .................................................................................................................... 52

4.9 SEM picture of e-spun LLDPE fiber with 22% concentration at magnification 2000 .................................................................................................................... 52

4.10 SEM of single electrospun LLDPE fiber showing the skin morphology ........... 54

4.11 SEM picture of e-spun LLDPE fiber on 22% concentration with graphene at magnification 1000 ........................................................................................................................................ 55

4.12 SEM picture of e-spun LLDPE fiber on 22% concentration with graphene at magnification 2000 ........................................................................................................................................ 55

4.13 2D WAXD scans for electrospun fibers (a) concentration of 15% (b) concentration of 18% (c) concentration of 20% (d) concentration of 22% (e) bulk material..... 57

4.14 The representative curves of the scan intensity vs. equatorial 2θ angle for electrospun fibers at different concentration................................................................. 58

4.15 WAXS pattern of LLDPE fibers vs. LLDPE/graphene composite fibers .......... 62

4.16 Representative curves of the heat flow vs. temperature for the fibers electrospun with different polyethylene concentration.......................................................... 64

4.17 Representative curves of the heat flow vs. temperature for samples between 85 to 135º C................................................................................................................. 65

4.18 Representative curves of the heat flow vs. temperature for LLDPE/graphene fibers .................................................................................................................... 67

4.19 FTIR spectrums of LLDPE electrospun fibers. ..................................................... 68

4.20 Plots of stress vs. strain for 18 wt. % LLDPE fibers at various fiber diameters... 70

4.21 Plots of stress against strain for electrospun 22 wt. % LLDPE fibers at various fiber diameters............................................................................................................. 71

4.22 Plots of tensile modulus and tensile strength versus fiber diameter for 18% concentration fibers ........................................................................................................ 72
4.23 Plots of tensile modulus and tensile strength versus fiber diameter for 22% concentration fibers

4.24 Representative stress-strain curves of LLDPE/graphene composite fibers of different fiber diameter

4.25 Plots of tensile modulus versus fiber diameter for neat LLDPE and LLDPE/graphene

4.26 Plots of tensile modulus versus fiber diameter for neat LLDPE and LLDPE/graphene. All the fibers were spun from solution with 22 wt. % LLDPE
CHAPTER I

INTRODUCTION

Recently, one-dimensional nanostructures, such as nanotubes and nanofibers have been developed due to their unique properties and potential application. Electrospinning as an emerging technology of ultrafine fiber fabrication was patented by Anton Formhals in 1934 and has been undergoing a renaissance in the past decade [1-3]. Electrospun fibers with diameters ranging from a few tens to thousands of nanometers attract much interest because of their applications, such as nanocomposites, filtration media and tissue scaffolds [4-5].

A wide variety of polymers have been electrospun into nanoscale fibers using a simple laboratory instrument, but polyolefin is largely absent from the list. Electrospinning polyethylene is challenging due to their poor electrical conductivity and the lack of an appropriate solvent at room temperature. Thus, only a few reports have appeared on the electrospinning of PE to date [6-9].

In this study, linear low density polyethylene (LLDPE) and LLDPE/ graphene composite fibers were produced with diameters in the range of a few hundred nanometersto several micrometers. The morphology of the fibers was analyzed using
scanning electron microscopy (SEM). The crystallite structure such as crystallite size of the spu fibers is examined by using wide angle X-ray diffraction (WAXD). The degree ofcrystallinity is analyzed by DSC. The mechanical properties of single electrospun fibers are evaluated by Nano bionix.

The results suggested that the degree of crystallinity of electrospun LLDPE fibers is enhanced as the solution concentration increased, resulting in fibers with improved mechanical properties. Incorporation of high strength and high aspect ratio graphene into the fiber matrix improved the mechanical properties. In addition, both LLDPE fibers and LLDPE/graphene fibers exhibited an abrupt shift in tensile performance with fiber diameter decreased.
2.1 The Essence of Polyethylene

Polyethylene is a thermoplastic polymer which consists of a long backbone of covalently linked carbon atom with a pair of hydrogen atoms attached to each carbon. The chain end is terminated with methyl groups. The schematic structure is shown in Figure 2.1

![Figure 2.1 Chemical structure of pure polyethylene](image)

Polyethylene is created through polymerization of ethylene. The formula is \( \text{C}_2\text{H}_4\text{n}+2 \), where \( n \) is the degree of polymerization. Typically, the degree of polymerization is in the
range of 100 to 250,000. The corresponding molecular weight arise from 1400 to more than 3,500,000. Unlike other conventional organic materials which consist of identical molecules, polyethylene resins are composed of backbone in a wide-range length.

2.1.1 Classification of Polyethylene

Polyethylene is classified into several different categories based on its density and branching. The mechanical properties of PE significantly depend on molecular weight, the type and extent of branching, the crystal structure. Branches and other defect limit the crystallinity level of polyethylene in the solid state. Chains with fewer defects have a higher degree of crystallinity. Today’s commercial polyethylene is termed as (a) high density polyethylene (HDPE); (b) low density polyethylene (LDPE) (c) linear low-density polyethylene (LLDPE); (d) very low-density polyethylene (VLDPE)

a. High Density Polyethylene.

High density polyethylene (HDPE) primarily consists of unbranched molecules with very few flaws to break its linearity. The schematic representation of high density polyethylene is shown in Figure 2.2 HDPE has a density of greater or equal to 0.94 g/cm³ [10]. This value is higher compared with other types of polyethylene because HDPE with extremely low level defects can achieve a high degree of crystallinity. HDPE can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts.
HDPE is used in products and packaging such as detergent bottles, garbage containers and water pipes.

![Schematic representation of high density polyethylene](image1)

**Figure 2.2** Schematic representation of high density polyethylene

b. Low Density Polyethylene.

Low density polyethylene (LDPE) has branches consisting of ethyl and butyl together with long chain branches which occur at random intervals along the length of the main chain. The long-chain branch themselves can in turn be branches. Fig 2.3 shows schematic structures of LDPE. The density of LDPE typically falls in the range of 0.90-0.94 g/cm3 [11]. It is the numerous branches characteristic inhibit the ability of LDPE to crystallize, reducing the density relative to LDPE. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap.

![Schematic representation of low density polyethylene](image2)

**Figure 2.3** Schematic representation of low density polyethylene
c. Linear Low Density Polyethylene

Linear low density polyethylene (LLDPE) has short alkyl groups attached to the linear polyethylene backbones at random intervals. It is produced by the copolymerization of ethylene with 1-alkenes. To some extent the branches impede the crystallization, which reduces density relative to HDPE. LLDPE has a density range of 0.90–0.94 g/cm³ [12]. The general structure of LLDPE is shown in Figure 2.4

![Figure 2.4 Schematic representation of linear low density polyethylene](image)

d. Very Low Density Polyethylene

Very low density polyethylene has higher concentration of short-chain branches compared with linear low density polyethylene. The general structure of very low density polyethylene is shown in Fig 2.5. The high level of branching limits the crystallization, which is reflected in the very low density in the range of 0.86–0.90 g/cm³.
2.1.2 Crystal Morphology and Crystallization

2.1.2.1 Three-phase Morphology

Most polyethylene is semicrystalline. Semicrystalline polymers are those consisting of two or more solid phases, in at least one of which molecular chain segments has a regular three-dimensional organization. Polyethylene is composed of three-phase morphology in the solid state. Figure 2.6 is the schematic representation of the three phases contained in solid state.
The ordered phase of polyethylene consists of crystallites, whose thickness typically varies from 80 Å to 200 Å with lateral dimensions of up to several micrometers. The noncrystalline regions are in the range of 50-300 Å [13]. The third phase which lies between the crystalline region and disordered region is named as interfacial region. It is very important since it serves as a link to the other regions. Without this character, polyethylene would be a weak material.

Normally, the extended length of a common polyethylene molecular is up to 10,000 Å [14-15], which exceed the thickness of a crystallite. So any given molecule must transverse crystalline or noncrystalline regions many times. This property connects the crystalline, intercrystalline and noncrystalline zones together and makes interfacial region
exhibit varying degrees of order. There are three types of configurations known as “tie chains”, “loops” and “cilia” which are shown in Figure 2.7. And the ratio of chains returning to the same crystalline zone versus those spanning the disordered regions is related to the physical properties of the polyethylene.

![Figure 2.7 Tie chains, loops, and cilia in the noncrystalline phases of polyethylene](image)

2.1.2.2 Crystal Unit Cells

The crystal structure of a material can be described in terms of its unit cell, which stacked in three-dimensional space describes the bulk arrangement of atoms of the crystal. The length of axes of unit cell are designated a, b and c, and the angles between faces, α,
β and γ. Figure 2.8 illustrated a generic unit cell. Unlike the nonpolymeric material, polymeric unit cells contain short segments from one of more molecular chains.

Polyethylene can be constructed from three types of unit cells--orthorhombic, monoclinic, and hexagonal. The orthorhombic unit cell is the most common component [16-18].

Figure 2.8 Generic unit cell
Orthorhombic Unit Cell

The orthorhombic unit cell has axes with different length, while the angles between adjoining faces are 90 °C. The dimensions of the a, b, and c axes of high density polyethylene unit cell are 7.417, 4.945, and 2.547 Å respectively [19-21]. The dimensions of low density polyethylene and linear low density polyethylene have larger a and b axis dimensions than high density polyethylene with c axis remained constantly. The orthorhombic unit cell is illustrated in Figure 2.9.

Figure 2.9 Polyethylene orthorhombic unit cell (a) Orthogonal view; (b) view along c axis [22]
Monoclinic Unit Cell

The monoclinic crystal form is a metastable phase formed under sheer stress, such as cold working [23]. The lattice constants of the monoclinic structure are 8.09, 2.54 and 4.79 Å for a, b and c respectively. It can be reverted to the orthorhombic form when temperature is over 60-70 °C [24]. The configuration of monoclinic unit cell is shown in Figure 2.10

![Figure 2.10 Polyethylene monoclinic unit cell [22]](image-url)
Hexagonal Unit Cell

In polyethylene, hexagonal phase can be induced by suitably high temperatures and pressures. The lattice parameters of hexagonal are as follow: $a= 8.46 \text{ Å}$, $b=4.88 \text{ Å}$ and $c=2.45 \text{ Å}$ [25-26]. Figure 2.11 show the configuration of the hexagonal unit cell.

Figure 2.11 Polyethylene hexagonal unit cell [22]
2.2 Graphene

2.2.1 Properties of Graphene

Graphene is a two-dimensional sheet composed of sp\(^2\) carbon atoms arranged in a honeycomb structure. Figure 2.12 shows the Graphene structure of single two-dimensional hexagonal sheet of carbon atoms. It could be taken as the building block of all other graphitic carbon allotropes with different dimensionality. For example, graphite is made of graphene sheets stacked on top of each other and separated by 3.37\(\text{Å}\). Carbon nanotubes (CNT) can be made by rolling graphene sheets.

![Graphene structure](image)

Figure 2.12 Graphene structure of single two-dimensional hexagonal sheet of carbon atoms
The production of graphene nanosheets was firstly attained in 1970 [27]. And the isolation of single-layer graphene is achieved in 2004, by separating from graphite using micromechanical cleavage [28]. Graphene sheets have several exceptional properties. Single-layer graphene is the strongest material ever, which has 1 TPa Young’s modulus and ultimate strength of 130 GPa [29]. It has a thermal conductivity of 5000 Wm⁻¹ K⁻¹ [30]. Moreover, single-layer graphene has electrical conductivity up to 6000 S/cm [31]. In addition, graphene sheets possess extremely high surface area and gas impermeability [32]. All of these indicate graphene sheets have a great potential for improving mechanical, thermal and electrical properties of materials.

2.2.2 Graphene/polymer nanocomposites

Dispersion of graphene is a crucial step in production of graphene/polymer nanocomposites. Well dispersion ensures a maximized reinforced surface area, which will influence the neighboring polymer chains and, consequently, the properties of the whole matrix. Therefore, large efforts have been made to achieve a homogeneous and well-dispersed system. Most graphene/polymer composites have been developed by either reduced or unreduced graphene oxide using the following strategies: 1) solvent processing, 2) in situ polymerization and 3) melt processing.

Graphene oxide-based nanoparticles can offer the potential to combine several properties. Graphene oxide-derived fillers can present high electrical conductivities (on the order of thousands of S/m) [33], high modulus (reported values ranging from 208
GPa [34] to over 650 GPa [35]). But these reported values are generally lower than those reported for single-walled carbon nanotubes, which properties may be comparable to those of pristine graphene [36,37].

2.2.3 Production of graphene

There are various methods developed for graphene preparation, including micromechanical cleavage, epitaxial growth [38], thermal exfoliation of graphite oxide [39], gas phase synthesis [40, 41] and chemical reduction of graphene oxide [42-44]. Although the micromechanical cleavage method was used for the isolation of graphene from natural graphite [45], it is still evaluated as a model technique for basic research.

**Exfoliation and Cleavage**

It is possible to produce graphene from high purity graphite sheets. Graphite can be viewed as stacked layers of many graphene sheets, bonded together by weak inter-layer van der Waals force energy of about 2 eV/nm². The order of magnitude of the force required to exfoliate graphite is about 300 nN/µm² [46], which could easily be achieved by either mechanical or chemical method. The simple yet crucial experiment developed by Novoselov and Geim is using common adhesive tape to repeat the stick and peel process for several times, which finally brings a 1 lm thick graphite flake to a monolayer graphene [47]. In a little different approach, Hernandez et al. produce single- to few-layer graphene sheets through dispersion and exfoliation of pure graphite in N-methylpyrrolidone [48]. A similar method was later used by Lotya et al. to exfoliate the
graphite into graphene, which is achieved by dispersion of graphite powder in sodium
dodecylbenzene sulfonate (SDBS), followed with sonication [49]. There are many such
attempts to produce graphene either from graphite or graphite oxide powder and using
different solvents [50-52].

**Thermal decomposition and chemical vapor deposition**

Synthesis of graphene through thermal chemical vapor deposition (CVD) was first
reported on planar few layer graphene (PFLG) in 2006 [53]. In this work, camphor was
used as a precursor to synthesize graphene on Ni foils. Camphor was first evaporated at
180 °C and then pyrolyzed in another chamber at 700 to 850°C with argon as the carrier
gas. Then few-layer graphene sheets were observed on the Ni foils after cooling in the
room temperature. The produced graphene was found to have multiple folds and
estimated to have approximately 35 layers of graphene sheets. Later after understanding
of the mechanism of graphene growth, several research groups reported of growing
graphene on a large scale [54-55].

**Plasma Enhanced Chemical Vapor Deposition Techniques**

The earliest report of plasma enhanced chemical vapor deposition (PECVD) is by
Obraztsov et al., which proposed a dc discharge PECVD method to produce
nanostructured graphite-like carbon [56]. But the film produced with this method looks
thicker at most of the places. The first report on single-to few-layer graphene by PECVD
was found in 2004 [57-58]. Graphene was synthesized on a variety of substrates (Si, W, Mo, Zr, Ti, Hf, Nb, Ta, Cr, SiO2 and Al2O3) with a radio frequency PECVD system, without any surface preparation or catalyst deposition.

**Other Processing Routes**

Besides these main processing routes, there have been attempts to produce graphene through many other techniques, such as chemical methods, thermal decomposition [59-60].

2.3 Polymeric nanofibers

2.3.1 Electrospinning set up and process

Electrospinning is a method which utilizes the electrical charge to produce very thin fibers. It was first introduced by Formhals in 1934 [61]. Since 1990’s, more interests have been grown rapidly, to which Reneker [62-63] has made significant contributions. An electrospinning setup basically consists of three components: a high voltage supplier, a capillary tube, and a collector. In the process, the polymer solution is usually connected to the high voltage in the range of 5 to 35 kV. A jet is ejected from the surface of the solution when the applied electrical force overcomes the surface tension. Under the influence of electric field, the jet undergoes a series of electrically driven bending instabilities [64-68]. The solvent in it evaporates before reaching the grounded collector. The result fibers have diameters ranging from a few nanometers to greater than 5 μm [62].
Taylor derived the equation for the critical voltage where the conical shape of the drop is formed and equilibrium between forces exists:

\[ V_c^2 = 4 \left( \frac{H^2}{L^2} \right) (\ln\left(\frac{2L}{R}\right) - 1.5) (0.117\pi R\gamma) \]  

(1)

where \( V_c \) is the critical voltage, \( H \) distance between the collector and the tip of the capillary, \( L \) length of capillary tube, \( R \) radius of capillary, and \( \gamma \) surface tension of the solution.

Fig 2.13 is a schematic diagram of electrospinning setup. So far, more than fifty different polymers have been successfully electrospun into ultra fine fibers. For most of the polymers, both the dissolution and the electrospinning are able to be conducted at room temperature with atmosphere condition. Besides polymers molten in high temperature can also be electrospun into nanofibers. The different is that electrospinning process has to be performed in a vacuum condition [69-71].
Figure 2.13 Schematic of the general laboratory setup used for an electrospinning experiment (a) image of the Taylor cone and (b) image of the bending instabilities [72].

2.3.2 Parameters of the Electrospinning Process

The electrospun fibers could be influenced by several parameters: (a) solution parameters, such as viscosity, conductivity, surface tension (b) The process parameters, such as distance between the pipette and the collector, applied voltage (c) The ambient parameters, such as temperature, humidity, and air flow
2.3.2.1 Solution Parameters

**Viscosity**

Not all solution can be electrospun with applied high voltage. The formation of electrospun fibers is primarily based on the viscosity and surface tension of the polymer solution. Only with proper viscosity of solution, the jet can travel as a jet to the grounded target. For solution with low viscosity, the jet might break up into droplets (known as electrospraying) as a result of insufficient surface tension. Also, the instability of flow caused by the high cohesiveness of the solution will result the impossibility of electrospinning. Fig 2.14 is SEM photographs of electrospun PEO nanofibers conducted by Fong [73]. In their experiments, the PEO polymer with concentrations of 1–4.5 wt. % was used.

![SEM images of electrospun nanofibers with beads from different polymer concentration solutions](image)

Figure 2.14 SEM images of electrospun nanofibers with beads from different polymer concentration solutions [73].
Fong [31] recognized that higher polymer concentration resulted in fewer beads. When the polymer concentration increased, the shape of the beads changed from spherical to spindle like.

The solution viscosity has great effects on the diameter of electrospun fibers. The increase in solution viscosity will result in larger diameter fibers. The experimental data and theoretical analysis [74] show that the fiber diameter depends allometrically on the solution viscosity in the form

\[ d \propto \eta^\alpha \]

where \( d \) is the average diameter of the electrospun fiber, \( \eta \) is the viscosity and \( \alpha \) is the scaling exponent. The exponent value might differ between different polymers.

**Conductivity**

The second important parameter effect the resulting electrospun fiber is the conductivity of solution. The dimensionless number \( Vq/\gamma R^2 \) may be used to qualitatively explain the morphologies of electrospun fibers. In the dimensionless parameter \( Vq/\gamma R^2 \), \( Vq \) means the driving force for the jet, in which \( q \) is the charge of the solution. \( \gamma R^2 \) indicates the surface free energy, in which \( \gamma \) is the surface tension and \( R \) is the radius of a Taylor cone droplet [75]. When \( Vq/\gamma R^2 > 1 \), the electric energy overcomes the surface free energy, resulting a jet of liquid ejected from the Taylor cone. The fiber is able to have smaller bead and thinner diameters as a result of increasing electric energy of solution.
**Evaporation of Solvent**

The evaporation of solvent can affect the morphologies of electrospun fibers. The evaporation of solvent is controlled by parameters such as the boiling point of the solvent, the solvent content, the distance between spinneret and collector, the flow rate of solution and the temperature of the working environment. When the solvent from solution evaporate, the polymer result the following three factors: (1) entanglement increases as the polymer concentration increases, which stabilizes the jet (2) surface charge increases, which reduces the jet diameter (3) heat transfer caused by evaporation, which causes the formation of fiber skin.
2.3.2.2 Electrospinning Process Parameters

Applied Voltage

It has been demonstrated that applied voltage is able to control the formation of fibers, such as diameters and morphology. Insufficient field strength could lead to bead defects in the spun fibers or even failure in formation of liquid jet. Deitzel et al. found that increasing the applied voltage was able to alter the shape of the pendent drop [76]. In their experiments, increasing the applied voltage resulted in the volume of the pendent drop decreased. It is schematically illustrated in the Figure 2.15. When voltage increased to the certain value, the Taylor cone was formed at the tip of the capillary.

![Figure 2.15 Schematic of the shape of pendent drop changed with increasing voltage](image)

Meechaisue et al. demonstrated in their electrospun poly (DTE carbonate) experiments that there was a certain range of electric field strengths to get bead free e-spun fibers. Either too weak or too strong field will lead to the formation of beaded fibers.
It also showed that the average fiber diameter change from 1.9 to 2.2 µm when increasing the applied voltage from 20 to 25 kV.

**Capillary Tip–Collector Distance**

The distance between the capillary tip and the collector affect the fiber characteristics by influencing the whipping or instability of the jet, the deposition time. The jet could have adequate time to dry and more whipping motion when the gap distance increased. In the study of electrospinning PEO fibers from Jaeger et al, the fiber diameter decreased from 19 to 9 µm after traveling distances changing from 1 to 3.5 cm [77].

**Flow Rate**

First, the flow rate should be enough to maintain the Taylor cone at the tip of the capillary [78]. Second, the flow rate can influence the structure of the resulting fibers. Megelski et al. demonstrated that both fiber diameter and pore size increase with increasing flow rate. Additionally, more bead defects appeared once the flow rate was too high, due to the inability of fibers to dry completely before reaching the collector. Incomplete fiber drying also leads to the formation of ribbon-like (or flattened) fibers as compared to fibers with a circular cross section.
2.3.3 Morphology and structure of electrospun nanofibers

Most fibers produced from semi-crystalline polymers by electrospinning display hierarchic structure. During the electrospinning process, a fraction of the chains contained in the fiber crystallizes to form lamellae, which consists of small crystals, while the remaining fraction forms the amorphous phase [79-81].

Under the shear and elongation forces, the lamellae are organized to form fibrils, while the tie chain molecules pass through the neighboring crystallites to form small-sized bundles. Also, the chain orientate along the fiber axis due to the shear stress [79]. This phenomenon has been observed by Lim et al. [80]. They found the densely packed lamellae and fibrillar structures existed in the fibers as shown in Figure 2.16.

Figure 2.16 Structural morphology of electrospun fibers displaying the densely packed lamellae and fibrillar [80]
Koombhongse et al. [82] suggest that the morphology of the fiber obtained is determined by a complex interaction between fluid flow, electrical forces, and solvent evaporation.

2.3.3.1 Molecular Orientation

Under the influence of an electrostatic field, polymer fluid jet experiences a high degree of elongation strain and shear force, which assists the macromolecular chains to alien along the fiber axis and results in fibers with a high degree of molecular orientation [83-86]. Many experiments convince the process of electrospinning can alter the intrinsic structural properties of the material. It has been found by Zong et al. [87] that the molecular chains in the electrospun PLLA fibers were highly oriented compared to the random-coil shape chains in the PLLA film. And the orientation extent is able to be quantified by X-ray diffraction analysis.

2.3.3.2. Crystallinity

The rapid evaporation of liquid jet results in an immediate formation of the fiber structure. So the molecules have less time to realign themselves and the stretched chains do not get enough time to form crystalline lamellae. Accordingly, less developed structures with lower crystallinity form in the fibers. Hence, it can be summarized that the crystallinity in the fibers is influenced by the rate of solvent evaporation [88, 89].

A contrary theory proposed that the crystallinity can be even higher than the unprocessed raw polymer. It has been reported by Lee et al. [90] and Reneker et al. [91]
that the development of crystallinity is inhibited specifically for rigid polymers with high glass transition values. But for ductile polymers, which have lower glass transition values and need longer time to crystallize.

The degree of crystallinity can be determined by a variety of methods, such as density, differential scanning calorimetry, and wide-angle X-Ray diffraction. Each method is based on a particular set of assumptions. No two methods produce identical results for all samples since each method investigates different crystal structure.

2.3.3.3 Effect of fiber diameter on structural properties

It is has been demonstrated by Zussman et al. [92] in their study that the electrospun fibers possess skin-core morphology. That is the properties of the skin characterized by the oriented layered planes are different from those of the core region, which characterized by random-coil chains. When the fiber diameter is reduced to some critical value, the size of the skin region becomes comparable to the overall diameter of the fiber. In addition, the oriented layered planes existed in the wall of the fiber unite, which affect the overall properties of the fiber. The experiment from Wong et al. [83] confirms that the alignment of the molecules in the direction of fiber axis is improved as the fiber diameter reduced. It is also demonstrated by the molecular dynamic simulations of Curgul [93]
2.3.4 Mechanical properties of electrospun nanofibers

The tensile properties of electrospun fibers are related to the fiber diameter, molecular geometry, molecular orientation and degree of crystallinity.

2.3.4.1. Effect of Structural Morphology on Tensile Properties

The tensile properties of the fibers are influenced by degree of crystallinity and crystalline structure. It is well known that semi-crystalline polymers consist of two phases. The soft phase, known as the amorphous phase, provides the elastomeric characteristics. The hard phase, known as the crystalline phase imparts dimensional stability to the array of molecules. The arrangement of these two phases determines the physical and the mechanical properties of the semi-crystalline polymers [80, 83-86]. During electrospinning, changes in the structural formation taking place in fibers, especially crystallinity and molecular orientation. So the deformation mechanisms in the intermediate scale fibers are entirely different from the deformation mechanism observed in bulk material.

Wong et. al. [83] investigated the tensile properties of electrospun fibers and the bulk polymer prepared by injection molding. The tensile behavior displayed by these two groups is significant different. The necking phenomenon exhibited by the bulk sample did not show in the electrospun fibers. This result is attributed to the oriented and stretched polymer chains in the fibers [94-95]. Similar results were demonstrated by Lu and coworkers [94].
2.3.4.2. Effect of Fiber Diameter on Tensile Properties

The mechanical strength and stiffness of electrospun fibers are improved when the diameter of spun fibers is reduced below the critical diameter [83-85]. Arinstein et al. [86] demonstrated that this phenomenon occurs when the size of the supramolecular structures of the fibers is analogous to the overall fiber diameter. The orientation of macromolecules present in the supramolecular structures of the amorphous phase plays a governing role in increasing the mechanical properties of the fibers. Upon increasing the fiber size, both the tensile strength and modulus decrease and the larger diameter fibers have a propensity to display bulk-like properties. This observation is important for the plausible applications of the electrospun nanofibers. Instead of merely considering these polymers as fibers, they could be treated as miniaturized high aspect components for sensors and devices. Being aware that a sudden change in properties occurs as the diameter decreases proposes that we cannot employ acquired measurements from bulk specimens for modeling devices at the nanometer scale level. The modulus or tensile strength of fibers with a diameter greater than 2 µm is not affected by electrospinning and could be treated as bulk-like properties. The enhanced properties of finer diameter fibers were credited to the gradual ordering of the molecular chains and modest increase in the crystallinity of the fibers. The size effect can also be attributed to the densely packed lamellae and fibrillar structures. In finer diameter fibers, the lamellae and fibrillar structures align themselves along the fiber axis, which plays a crucial part in enhancing the mechanical properties of fibers. The fibrillar structure possesses a high degree of molecular orientation and provides high resistance to axial tensile force.
2.3.5 History of Production of Polyethylene Fibers

Electrospinning of polyethylene is challenging due to lack of an appropriate solvent at room temperature. So only a few reports have appeared on the electrospinning of PE to date, which include high-density PE (HDPE), linear low density polyethylene (LLDPE) and ultra-high molecular weight polyethylene (UHMWPE). All of these are based on the deformation of a gel, melt, or solid polyethylene, ranging from the spinning of dilute solutions to melt spinning. The first attempt was to electrospin HDPE both from the melt at 200-220 °C and from a dilute solution in paraffin at 100 °C by Larrondo and Manley [96-98]. The resulting polyethylene fibers had diameters ranging from several microns up to several hundred microns. But this method is quite complicate since the solvent need to be removed by extensive washing in cold xylene. Figure 2.17 is SEM picture of HDPE fiber formed in the method mentioned above. The recently reported method for electrospinning LLDPE is from Givens et al. [99], in which PE fibers was prepared from p-xylene solution including a small amount of salt at 105 °C. The resulting fibers had large diameters and very rough surface morphology. Figure 2.18 is FESEM of LLDPE electrospun fiber at 3K and 15K magnification. The first report for electrospinning of UHMWPE is from Rein et al [100]. In this experiment, PE fibers with a minimum diameter of 200 nm were electrospun from a mixture of p-xylene and cyclohexanone at 120 °C. Figure 2.19 shows the micrographs of UHMWPE fibers electrospun from solutions mixture of p-xylene and CH in ratio of 1:1 at different UHMWPE concentrations. The most prominent technology is termed as gel spinning.
The commercial UHMWPE Dyneema® fibers are manufactured by means of gel-spinning process, which is the world’s strongest fiber, 15 times stronger than steel.

Figure 2.17 SEM of HDPE fiber formed in an electrically driven jet of 1% polyethylene in paraffin [96]

Figure 2.18 FESEM of LLDPE electrospun fiber at 3K and 15K magnification [99]
2.3.6 Application of electrospun nanofibers

Electrospinning is a simple and powerful technology for producing polymer nanofibers. Advantages of electrospinning over the conventional spinning method include a simple apparatus, the flexibility in material selection to electrospin and best of all, its capability of producing fibers with very high surface to volume ratio. The unique properties of electrospun nanofibers make them attractive for a number of applications, including tissue engineering, electrospun fiber reinforced composites and filtration.

2.3.6.1. Tissue Engineering Application

In the last decade, electrospinning has gained widespread interest for application in tissue engineering. The electrospun fibers with micro to nanoscale topology and high porosity are similar to the natural extracellular matrix. And the abilities of cell attachment, drug loading as well as mass transfer are largely improved due to the high surface to
volume ratio properties of e-spun fibers. The fact that electrospun fibers have random orientation and arrangement also help to control both the bulk mechanical properties and the biological response to the scaffold. Due to the flexibility in material selection as well as properties mentioned above, electrospun scaffolds have been employed in wide variety of tissue applications including: vascular [101-103], bone [104-105], and neural [106]. Application of electrospun fibers in tissue engineering often involves several considerations, including choice of material, fiber orientation, porosity and surface modification.

2.3.6.2. Electrospun Fiber Reinforced Composites

Although electrospun fibers show clear potential for developing fiber composite materials, the application is limited by difficulties in making sufficient quantities of fibers in an efficient way. For this reason, electrospun fiber reinforced materials are popular in medical application since it requires relative small amount.

The fracture toughness and fracture energy of the composite rely on the layout of the fibers in the composite [107]. Hence, the control of fiber orientation and the dispersion of the fibers in the matrix are the current issues associated with the application of electrospun nanofibers as reinforcement in composite. For a better reinforcement, the electrospun nanofibers need to be collected as a highly aligned yarn. And the dispersion could be improved if the fibers are trimmed into shorter fragments.
2.3.6.3. Filtration

Electrospun fibers have found potential applications in the filtration industry [108-110]. Due to the micrometer-sized diameters of fibers, London-Van Der Waals forces are main method of adhesion between the captured materials and fibers. Electrospun fibers have been investigated for air filtration applications. It is been shown that the filtration efficiency of the electrospun mats is as good as the commercially available filter. But the filter mass of the electrospun fibers is considerably lower than the commercial filter [111].
3.1. Material

The linear low density polyethylene (LL6201) was purchased from ExxonMobil Chemical, which has a density of 0.926 g/cm$^3$ and melt index 50g/10min. Cis- and trans-mixture decahydronaphthalene (decalin) was purchased from TCI America. Tert-butylammonium bromide (t-BAB) was purchased from Strem Chemicals.

3.2 Production of Graphene

The dispersion was prepared by sonication of graphite powder in acetone (0.1 mg ml$^{-1}$). The sonication was performed in the power sonic bath (Branson B300) for 2 hours. Figure 3.1 is the dispersion after sonication. To remove the graphite aggregates, centrifugation of the dispersion was carried out for 10 min at 10000 rpm (Thermo, IEC CL 30) immediately after sonication. A homogeneous dispersion of graphene was then
obtained by removing the top of the centrifuged dispersion. The dispersion need to be
dried in air for 2 days to removal of the remaining solvent.

Figure 3.1 Dispersion of graphene after sonication for 2 hours.

3.3 Electrospinning process

3.3.1 Fabrication of Linear Low Density Polyethylene fibers

An infrared (IR) heating system combined with a standard electrospinning setup was
used to perform high-temperature electrospinning experiments. The standard
electrospinning consists of a high-voltage power supply, a pipette, a grounded sheet of
aluminum foil. A 7.5 cm by 12.5 cm 500 W 110 volt ceramic infrared emitter with a
variable output 110 V controller was purchased from Mor Electric Heating Associates of
Comstock Park, MI. The IR emitter system remains at a given temperature with only
minor fluctuations. The infrared flux on the solution can be controlled by the distance
between the emitter and the pipette. This noncontact system still allows visual monitoring of solution conditions. Fig 3.2 is a schematic of the high temperature electrospinning setup.

![Fig 3.2 Schematic of the high temperature electrospinning setup](image)

Linear low density polyethylene pellets were dissolved in decalin by heating the mild stirred solutions for 3 hours at 120 °C in an oil bath. Once the polyethylene was fully dissolved, 0.5 wt % of t-BAB was added, and the solution was stirred for an additional 15 minutes. The resulting solutions were transferred to a pipette which was preheated to 115 °C. Electrospinning was performed at a voltage of 10KV. The gap distance between the tip of the pipette and the collector was set to 15cm. The distance between two emitters is 10
cm. And the pipette was set in the middle of them. Solution temperature was maintained at 105-110 °C. The fibers were dried in vacuum at 70 °C overnight prior to testing to vaporize the remaining solvent.

3.2.2 Fabrication of Linear Low Density Polyethylene fiber/ Graphene Composite Fibers

A two-step method was used for homogeneous dispersion of graphene into solution. First, graphene (1 wt% of LLDPE in the solution) were added to the solvent and sonicated for 3 h to disrupt any possible agglomerations. Second, 22 wt% of LLDPE were added to the solution, which was then heated in the oil bath at 120 °C for 3 hours with mild stirring. The electrospinning process was similar as the method mentioned for pure LLDPE. Figure 3.3 is the image of LLDPE/Decalin/ graphene dispersion

Figure 3.3 Image of LLDPE/Decalin/ graphene dispersion
3.4. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference.

Thermal properties of the electrospun linear low-density polyethylene (LLDPE) and LLDPE/graphene composite fibers were analyzed using a TA Instruments 2920 Modulated DSC (New Castle, DE) at a heating rate of 10 °C per minute from 40 to 200 °C under nitrogen gas atmosphere. Figure 3.4 is digital picture of the TA instruments DSC. Melting temperature (Tm) and crystallization (%) was determined for the samples. The percent of crystallinity for electrospun LLDPE and LLDPE/graphene samples were calculated as

\[
\% \text{ Crystallinity} = \frac{\Delta H_m}{\Delta H_o}
\]

Where \( \Delta H_m \) is the enthalpy of melting of LLDPE samples and \( \Delta H_o \) is the enthalpy of melting of fully crystalline LLDPE. Area under the melting peak of the thermogram was determined to be an estimate of \( \Delta H_m \).

Figure 3.4 Digital picture of the TA instruments DSC
3.5. Wide-Angle X-Ray Diffraction

Wide-angle X-Ray diffraction (WAXRD) refers to the scattering of X-rays over a range of angles ($\theta$) from about 2° to 180°. The well-regimented arrays of atoms in the crystalline regions scatter the X-rays at distinct angles, while the noncrystalline region diffuse scattering over a broad range of 2$\theta$ angles. Analysis of the well defined peaks can yield information of the unit cell dimension with an accuracy of four significant figures. And the larger and more regular the crystallites, the sharper will be the peaks.

On the analysis of the intensity distribution of the diffraction peaks, quantitative measurements of crystallite thickness and types of disorder can be achieved. The equation describing the angle at which a beam of X-rays of a particular wavelength diffracts from a crystalline surface was discovered by Sir William H. Bragg and Sir W. Lawrence Bragg.

$$2dsin \theta = n\lambda$$

$\lambda$ = wavelength of the x-ray

$\theta$ = scattering angle

$n$ = integer representing the order of the diffraction peak.

$d$ = inter-plane distance of (i.e. atoms, ions, molecules)

In the case of polyethylene, the most useful information lies in the range of 2$\theta$ angles from 5° to 50°, which corresponds to a range of atomic spacing on the order of 2 to 20 Å.
In this work, two-dimensional WAXD patterns of samples were obtained using a Rigaku X-ray imaging system which has an 18 kW rotating anode X-ray generator in the transmission mode. The X-ray hit the sample in a form of a circle with a diameter of 0.5 mm. Figure 3.4 Digital picture of the wide-angle X-Ray diffraction instrument.

Figure 3.5 Digital picture of the wide-angle X-Ray diffraction instrument
3.6. SEM Analysis

Scanning electron microscopy (SEM) was used for analyzing the surface morphology of the samples. All the samples are silver coated using a K575x sputter coater (Emitech Kent, England) in an argon purged chamber evacuated to 500 mTorr. The samples were mounted on an aluminum stub (15 mm height and 3mm diameter) using a double sided adhesive tape, then examined with an accelerating voltage of 20 kV using a JSM-6510LV/GS from JEOL (Ibaraki, Japan).

3.7. Diameter Measurement

The average fiber diameter was measured using the SEM micrograph and “Image J” software. At least one hundred randomly selected fibers were chosen to obtain the average diameter and standard deviation. For the single fiber, diameter needs to be measured at least five times. The average value is used to calculate the fiber area.

3.8 Fourier-Transform Infrared Spectroscopy (FTIR)

The Fourier transform infrared spectroscopy (FTIR) is widely used to study the nature of chemical bonds of polymers through the characterization of the vibration modes. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms. As each different material is a unique combination of atoms, infrared spectroscopy can result in a positive identification of every different kind of material. In addition, the size of the
peaks in the spectrum indicates the amount of material present. One can easily follow chemical and morphology transformations of the polymers subject to different constraints.

In my study, FTIR (Nicolet 380) is performed to measure the chemical structure of polyethylene. The samples are placed on top of an attenuated total reflection set and scanned from 400 to 4000 cm\(^{-1}\). With average 32 scans, the absorption spectrum is obtained. The resulting peaks obtained from the plots are analyzed and matched with known signatures of identified molecules.

3.9 Mechanical Testing

3.9.1 Sample preparation and tensile test

The stress vs. strain for e-spun LLDPE and LLDPE/graphene composite single fibers was conducted on ultra-sensitive testing equipment MTS Nano Bionix® (MTS Systems Corporation, Oak Ridge, TN, USA) with a load resolution of 50 nN and extension resolution of 35 nm. In order to collect single fiber, the fibers were first electrospun onto a grounded parallel aluminum frame. A single fiber was then selected and mounted onto cardboard fixed super glue as shown in figure 3.5. The gauge length of the fiber specimen was 11 mm. The cardboard was subsequently mounted onto MTS Nano Bionix®. The vertical sides of the cardboard were cut off before the test. The specimen was pulled at a constant strain rate of 0.01 s\(^{-1}\) until fracture. Figure 3.6 shows the instrument used for testing.
Figure 3.6 Preparation of single electrospun fiber for tensile test
Figure 3.7 Instrument used for testing: MTS Nano Bionix®.
CHAPTER IV

RESULTS AND DISCUSSION

4.1 SEM Analysis

The morphology of electrospun LLDPE fibers was analyzed using the SEM. Figure 4.2-4.9 show the SEM micrograph of LLDPE electrospun fibers with concentration at 15%, 18%, 20% and 22% respectively. The morphology of the electrospun fibers was found to vary with the concentration of the polymer solution. Since, electrospinning is conducted under identical conditions such as, temperature, voltage and tip-to-collector distance, this phenomenon can be explained only in terms of the different concentration.

Electrospinning was started from LLDPE content at 5 wt. %. However, electrospraying rather than electrospinning happened for solution with concentration below 15%. It was attributed to insufficient chain overlap. Solution at low concentration results in insufficient chain entanglement, which cannot withstand both the electrostatic and Coulombic repulsion forces acting on the charged jet. Thus, the charged jet was disintegrated into smaller entities, which surface tension subsequently minimizes the surface area. Hence discrete spheres were formed on the collector [112].
The transformation from beads to fibers began at 15 wt. % LLDPE solution (Figure 4.2-4.3). But beads with oblong shape appeared in the fibers and the average fiber diameter was $0.75 \pm 0.40 \, \mu m$. The sizes and number of beads decreased dramatically and the fiber average diameter increased to $1.17 \pm 0.34 \, \mu m$ as LLDPE concentration was increased to 18 wt. %. Further increasing the solution concentration to 20 wt. % and 22 wt. % resulted in the formation of smooth fibers. It is attributed to the high chain entanglement, which completely prevent the charged jet from disintegration. In addition, higher polymer concentration resulted in fibers with larger diameters. It could be explained by increased viscoelastic force that opposes the stretch induced by the Coulombic repulsion force.

The concentration dependence of the electrospun fiber diameter is summarized in Figure 4.1. It indicates that the fiber diameter increase with the concentration increased.

![Figure 4.1 Plot of the variation of average fiber diameter vs. concentration](image.png)
Fig 4.2 SEM picture of e-spun LLDPE fiber with 15% concentration at magnification 1200

Fig 4.3 SEM picture of e-spun LLDPE fiber with 15% concentration at magnification 2000
Fig 4.4 SEM picture of e-spun LLDPE fiber with 18% concentration at magnification 1200

Fig 4.5 SEM picture of e-spun LLDPE fiber with 18% concentration at magnification 2000
Fig 4.6 SEM picture of e-spun LLDPE fiber with 20% concentration at magnification 1200

Fig 4.7 SEM picture of e-spun LLDPE fiber with 20% concentration at magnification 2000
Fig 4.8 SEM picture of e-spun LLDPE fiber with 22% concentration at magnification 1200

Fig 4.9 SEM picture of e-spun LLDPE fiber with 22% concentration at magnification 2000
Figure 4.10 is a SEM micrograph of single electrospun LLDPE fiber. It has been observed that when the concentration of solution increased, the resulting fiber formed less dense skin. The characteristic skin formation of electrospun fibers can be attributed to capillary flow mechanism. When a drop of solution dries on a substrate, the resulting outward flow can carry the dispersed material to the edge although which are initially homogeneously dispersed over the entire dispersion [113]. For electrospinning process, solvent at the fiber surface evaporates first, then replenished by liquid from the interior. The resulting outward flow can carry the dispersed polymer molecular to the perimeter of the droplet. Thus, characteristic skin made up of ingredients is achieved after complete evaporation of solvent. In dilute polymer solutions with low viscosity, evaporation of solvent on the external layer of fiber leaves a dense skin. On the other hand, the effect of evaporative flow for high polymer concentration solution is not as strong as in the dilute solution. Thus, only limited amount of polymer molecules can be carried to the boundary and the surface results in a thin skin layer.
Figure 4.10 SEM micrograph of single electrospun LLDPE fiber showing the skin morphology

Figure 4.11 and 4.12 are the SEM micrographs for electrospun LLDPE/graphene composite fibers. The electrospinning for composite fibers are conducted under the same condition as the pure LLDPE fibers. The polymer solution at 22 wt. % is added with graphene at 1 wt. % of polyethylene in it. The average diameter is $1.32 \pm 0.49 \, \mu m$, which is smaller compared with pure LLDPE fibers. The electrical conductivity of the solution was increased when the conductive graphenes were present in the solution. Thus, the reduced fiber diameter for composite nanofibers is presumably due to increased stretching of the fiber during electrospinning process.
Fig 4.11 SEM picture of e-spun LLDPE fiber on 22% concentration with graphene at magnification 1000

Fig 4.12 SEM picture of e-spun LLDPE fiber on 22% concentration with graphene at magnification 2000
4.2 WAXD analysis

X-ray analysis was performed on electrospun LLDPE fibers with different concentration to study the crystalline structure. The obtained 2D WAXD scans are shown in Figure along with the one for a film compression molded from bulk.
Figure 4.13 2D WAXD scans for electrospun fibers (a) concentration of 15% (b) concentration of 18% (c) concentration of 20% (d) concentration of 22% (e) bulk material

The representative curves of the scan intensity vs. equatorial 2θ angle are shown in Figures 4.14. Although LLDPE electrospun at different concentration, two principal reflections are observed in all cases, which are 2θ scan radian of 21.6° and 23.8°. These two distinct peaks correspond to the (110) and (200) lattice planes of the orthorhombic phase of polyethylene crystals, respectively.
Figures 4.14 Representative curves of the scan intensity vs. equatorial 2θ angle for electrospun fibers at different concentration

The crystallite size of a given reflection was calculated using the Scherrer equation.
\[ L_{(hkl)} = \frac{k \lambda}{L \cos \theta} \]

where \( \theta \) is the Bragg angle for the reflection concerned, \( \lambda \) is the wavelength of radiation (1.542 Å), \( L_{(hkl)} \) is the mean length of the crystallite perpendicular to the planes (hkl), \( \beta \) is either the integral breadth or the breadth at half maximum intensity in radians, and \( K \) is a Scherrer parameter, which is always taken as 0.9 when \( \beta \) is the full width at half maximum (FWHM) and 1.0 when \( \beta \) is the integral breadth.

The result is shown in table 4.1. The \( d \)-spacing values of these reflections match an orthorhombic type of unit cell (4.10 and 3.70 Å respectively) [113]. The result also indicated that as the concentration increased, the crystallite size decreased. It has been demonstrated by the DSC analysis that the crystallinity increased as the concentration increased. So it can be concluded that the crystallite size slightly decreased as the crystallinity increase. This phenomenon has been observed in other experiments. After irradiation of UV, \( \gamma \)-rays or other high-energy electronic beams, the crystallinity of the UHMWPE fiber was increased but the crystallite size was decreased. [114-119]
TABLE 4.1 X-ray Diffraction Analysis Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Indexing</th>
<th>d-spacing (Å)</th>
<th>Peak Position (2θ°)</th>
<th>Half-height width (2θ°)</th>
<th>Crystallite size(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15%</td>
<td>110</td>
<td>4.1682</td>
<td>21.299</td>
<td>0.680</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.7592</td>
<td>23.648</td>
<td>0.769</td>
<td>106</td>
</tr>
<tr>
<td>18%</td>
<td>110</td>
<td>4.1972</td>
<td>21.150</td>
<td>0.662</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.7825</td>
<td>23.500</td>
<td>0.626</td>
<td>135</td>
</tr>
<tr>
<td>20%</td>
<td>110</td>
<td>4.1871</td>
<td>21.201</td>
<td>0.596</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.7744</td>
<td>23.551</td>
<td>0.585</td>
<td>146</td>
</tr>
<tr>
<td>22%</td>
<td>110</td>
<td>4.273</td>
<td>21.190</td>
<td>0.624</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>4.1307</td>
<td>23.450</td>
<td>0.558</td>
<td>155</td>
</tr>
<tr>
<td>Hot pressed film</td>
<td>110</td>
<td>4.1391</td>
<td>21.450</td>
<td>0.565</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.7433</td>
<td>23.750</td>
<td>0.661</td>
<td>104</td>
</tr>
</tbody>
</table>

The result from this work is consistent with the one reported for commercial UHMWPE fiber SPECTRA® [120]. The crystallite sizes perpendicular to the 110 and 200 of the orthorhombic structure for commercial UHMWPE fiber SPECTRA® are listed in Table 4.2.
TABLE 4.2 X-ray Diffraction Analysis Results [120]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Indexing</th>
<th>Observed d-spacing</th>
<th>Peak position (2θ)</th>
<th>half-height</th>
<th>L(hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPECTRA® 900</td>
<td>110</td>
<td>4.103</td>
<td>21.658</td>
<td>0.69</td>
<td>129.8</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.698</td>
<td>24.064</td>
<td>0.71</td>
<td>126.6</td>
</tr>
<tr>
<td>SPECTRA® 1000</td>
<td>110</td>
<td>4.115</td>
<td>21.593</td>
<td>0.62</td>
<td>144.8</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.732</td>
<td>23.481</td>
<td>0.86</td>
<td>104.7</td>
</tr>
<tr>
<td>SPECTRA® 1200</td>
<td>110</td>
<td>4.049</td>
<td>21.953</td>
<td>0.66</td>
<td>135.5</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.712</td>
<td>23.973</td>
<td>1.05</td>
<td>86.1</td>
</tr>
</tbody>
</table>

Crystalline structures of the LLDPE/graphene fibers were also studied by WAXS. Figure 4.15 is the representative curves of the scan intensity vs. equatorial 2θ angle, which displays two main peaks for all samples at 2θ scan radian of 21.6° and 23.8°. The WAXS patterns of the fibers with graphene are similar to that of unfilled LLDPE fibers, revealing that the composite fibers contain only orthorhombic phase.
Figure 4.15 WAXS pattern of LLDPE fibers vs. LLDPE/graphene composite fibers
4.3 DSC analysis

Electrospun fibers were studied by DSC analysis in order to determine the crystallinity and their $T_m$. All the samples were heated from 40 °C to 200° C at a rate of 10 °C/min. Figure 4.16 shows representative curves of the heat flow vs. temperature for the fibers electrospun with different polyethylene concentration and the sample from bulk.

For the bulk LLDPE, a single endothermic peak is observed. The melting peak onset and end-set temperatures were 72° ± 1° C and 134° ± 1° C respectively. The apex of the peak ($T_m$) was 126° ± 1° C.

The endothermic curves obtained from electrospun LLDPE fibers present a main melting peak with apex ($T_m$) at about 124 ± 1° C and one weak peak at lower temperatures. The main melting peak became shaper when the solution concentration increased. When the concentration was over 20%, a shoulder was observed in the main melting peak. Figure 4.17 is the representative curves of the heat flow vs. temperature for samples between 85 to 135° C, which shows the changes of the endothermic peaks more clearly.

Since there was only one sharp peak observed in the endothermic curve of LLDPE, the multiple peaks must correspond to the crystallization conditions in the electrospun fibers. The peak at lower temperature reveals that distinct crystallite fractions were formed in the process of high temperature electrospinning. The peaks of endothermic curves became sharper as the concentration increased, which indicated more crystallinity in the samples. It is owing to the fact that more concentrated solution accompanied with
an increasing of number of entangled molecular chains, which increases the interaction force between polymer chains, contributes to increase in crystallinity [121].

Figure 4.16 shows representative curves of the heat flow vs. temperature for the fibers electrospun with different polyethylene concentration
Figure 4.17 Representative curves of the heat flow vs. temperature for samples between 85 to 135°C
Table 4.3 is the results from the thermal analysis. The melting point is determined as the last, highest - temperature points of the melting endotherm, since this is the temperature at which the most perfect crystallites melt. The heat fusion ($\Delta H_m$) of crystalline phase was calculated by using the following equation. The crystallinity of the samples was estimated by assuming that $\Delta H_o$ (100% crystallinity) is 290J.g$^{-1}$[122]

$$\text{% Crystallinity} = \frac{\Delta H_m}{\Delta H_o}\]$$

Table 4.3 Thermal analysis results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melt Onset Temperature (ºC)</th>
<th>Melt Peak Temperature (ºC)</th>
<th>Enthalpy(J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15%</td>
<td>115.99</td>
<td>124.38</td>
<td>84.2</td>
<td>28.7</td>
</tr>
<tr>
<td>18%</td>
<td>109.57</td>
<td>124.38</td>
<td>116.4</td>
<td>39.7</td>
</tr>
<tr>
<td>20%</td>
<td>100.26</td>
<td>125.32</td>
<td>124.0</td>
<td>42.3</td>
</tr>
<tr>
<td>22%</td>
<td>120.69</td>
<td>124.29</td>
<td>147.7</td>
<td>50.4</td>
</tr>
<tr>
<td>Hot pressed film</td>
<td>116.29</td>
<td>125.80</td>
<td>120.8</td>
<td>41.2</td>
</tr>
</tbody>
</table>
Figure 4.18 shows representative curves of the heat flow vs. temperature for LLDPE/graphene fibers. For comparison, the endothermic curve of the pure LLDPE fiber was included in the figure.

The melting peak onset and end-set temperatures were $110^\circ \pm 1^\circ$ C and $123^\circ \pm 1^\circ$ C respectively. The apex of the peak ($T_m$) was $123^\circ \pm 1^\circ$ C. The calculated crystallinity is 47.2%, which is lower than the fibers without graphene.

Figure 4.18 Representative curves of the heat flow vs. temperature for LLDPE/graphene fibers
4.4 FTIR analysis

The spectra of different types of electrospun polyethylene required in form of film are shown in Figure 4.18. The result indicates that all samples present the same absorptions, varying only in terms of intensity, which can be attributed to differences in film thickness.

![FTIR spectrums of LLDPE electrospun fibers](image)

Figure 4.19 FTIR spectrums of LLDPE electrospun fibers

Main absorptions of polyethylene in the IR region and their assignment are reported in Table I.
FTIR analysis (Figure 4.19) indicates the strong CH2 asymmetric stretching band at 2919 cm\(^{-1}\) and the CH2 symmetric stretching band at 2851 cm\(^{-1}\) along with the CH2 bending at 1465 cm\(^{-1}\) and rocking deformation at 725 cm\(^{-1}\)[123].

The CH stretching positions indicate conformational ordered -CH2- chains and the splitting of the -CH2- scissors vibration is indicative of the intermolecular interaction of two chains in an orthorhombic unit cell [124]. These data confirm the existence of orthorhombic crystalline form in the electrospun material, which is consistent with the crystalline conformation found in the bulk material. The high temperature electrospinning process did not alter the chemical structure of the material.

**TABLE 4.4 Main absorption bands of polyethylene and their assignments**

<table>
<thead>
<tr>
<th>Band (cm(^{-1}))</th>
<th>Assignment*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2919</td>
<td>CH2 asymmetric stretching</td>
</tr>
<tr>
<td>2851</td>
<td>CH2 symmetric stretching</td>
</tr>
<tr>
<td>1473 and 1463</td>
<td>CH2 bending deformation (A)</td>
</tr>
<tr>
<td>731–720</td>
<td>Rocking deformation</td>
</tr>
</tbody>
</table>
4.5 Tensile testing

4.5.1 Mechanical properties of electrospun LLDPE fibers

In order to study the effect of the concentration on their tensile properties, single electrospun LLDPE fibers were subjected to tensile testing under the same condition. Figure 4.20 and Figure 4.21 show representative stress-strain curves as a function of fiber diameter at 18\% and 22\% concentration respectively. All the samples demonstrate similar trend in their stress-strain behavior, without any necking phenomenon. The mechanical properties were found to vary with fiber diameter. The tensile strength decreased with increase in fiber diameter, while the strain at break was found to increase with in fiber diameter increased.

![Stress vs Strain Plot](image.png)

Figure 4.20 Plot of stress vs. strain for 18 wt. \% LLDPE fibers at various fiber diameters.
Figure 4.21 Plot of stress against strain for electrospun 22 wt. % LLDPE fibers at various fiber diameters.

Figure 4.22 and Figure 4.23 are the plots of tensile modulus and tensile strength versus fiber diameter, respectively. The modulus and strength of the fibers increases as the fiber diameter decreases and there is a sharp increase in both modulus and strength value when the fiber diameter decreases to less than 1.2 μm. The abrupt increases in modulus and tensile strength values of electrospun fibers due to the size effect are also reported by Arinstein et al. [125], Lim et al. [80] and Chew et al. [126].
Figure 4.22 Plots of tensile modulus and tensile strength versus fiber diameter for 18% concentration fibers
In this study, the modified Hall-Petch equations are used to show that fiber modulus and strength are influenced by the fiber diameter. The relationships are given by

\[ M = M_0 + \frac{\chi}{d^\alpha} \]  

\[ S = S_0 + \frac{\kappa}{d^{\beta}} \]  

where \( M_0 \) and \( S_0 \) represent the modulus and strength at large \( d \); \( \chi \) and \( \kappa \) are material constants.

Figure 4.23 Plots of tensile modulus and tensile strength versus fiber diameter for 22% concentration fibers
Hall-Petch equation for 18 wt. % (4-5) and 22wt. % (5-6) are shown as follow

\[
M = 0.011 \frac{23.63}{d^{1.11}} 
\]  
(3)

\[
S = 1.94 \frac{12.08}{d^{1.77}} 
\]  
(4)

\[
M = 0.058 \frac{45.62}{d^{1.59}} 
\]  
(5)

\[
S = 0.0609 \frac{16.44}{d^{1.12}} 
\]  
(6)

The variation of mechanical properties with the fiber diameter observed in this study can be explained by deformation mechanisms introduced by electrospinning process. Usually, the process of drawing results in fibers with higher strength and stiffness. When the polymer jet travels from the capillary to the collector, bending instability occurred and the jet stretches to a greater extent under the electric field. The narrowing of the jet is analogous to the drawing process of gel or melt spun fibers, which reduces fiber diameter, stretches molecular chains and increases the orientation of macromolecular chains along the fiber axis. So the fibers with smaller diameters undergo more stretching during the process and exhibit better mechanical properties.

The value of modulus and strength of the LLDPE fibers reported in this study is not as high as respected. It can be also explained by the electrospinning process. It has been observed that, compared with other electrospun fibers there were less fiber whipping
action appeared during the process. Less whipping action can reduce the drawing ratio
during spinning, which could be the source of the larger diameter fibers and results the
fiber with lower values of modulus and strength. In addition, the solution cooled
immediately after leaving the Taylor cone, which caused the rapid onset of crystallization.
Therefore, the polymer jet did not get enough time to form crystalline lamellae, which
could be another source for poor mechanical properties.

4.5.2 Mechanical properties of electrospun LLDPE/graphene composite fibers

Figure 4.24 shows representative stress-strain curves of electrospun
LLDPE/graphene composite fibers as function of fiber diameter determined from the
tensile tests. All the samples display similar trend in their stress-strain behavior. The
deformation behaviors of these composite nanofibers are consistent with the deformation
mechanisms of pure LLDPE fibers.
Figure 4.24 Representative stress-strain curves of LLDPE/graphene composite fibers of different fiber diameter.

Figure 4.25 and 4.46 show the plots of tensile modulus and tensile strength versus fiber diameter, respectively. Both the neat LLDPE and LLDPE/graphene composite fibers were electrospun from solution at 22 wt. % concentrations. The difference is the composite fibers adding 1 wt. % of the LLDPE content into the solution. The electrospinning for all samples are conducted under the same condition.

The modulus and the strength of the composite fiber also exhibit the size effect. That is the modulus and strength of the fibers increase as the fiber diameter decreases, while an abrupt change in tensile modulus and strength exhibit in the proximity of 1\( \mu \text{m} \) in
diameter. The modified Hall–Petch equation was also used to develop a relationship between tensile modulus and strength vs. fiber size. The fitting equation is:

\[
M = 0.0677 + \frac{85.88}{d^{1.84}}
\]  

(7)

\[
S = 0.0211 + \frac{25.32}{d^{1.32}}
\]  

(8)

Figure 4.25 Plots of tensile modulus versus fiber diameter for neat LLDPE and LLDPE/graphene.
Figure 4.26 Plots of tensile modulus versus fiber diameter for neat LLDPE and LLDPE/graphene. All the fibers were spun from solution with 22 wt. % LLDPE.

The thermal analysis indicates the crystallinity of neat polymer is 50.4%, which is higher than composite values at 47.2%. So the significant improvements in both modulus and strength of the composite fiber can be only explained by the reinforcement effect of graphene on the matrix.

It has been reported that molecular and geometrical factors play pivotal roles on the strengthening and toughening of materials in the nanometer length scale [28-29]. The addition of graphene presents an extra interface for molecular chains orientation. Thus, CNTs reduce the mobility of the polymer chains and limit their segmental motion, which help strengthen the fibers. The influence is more evident for the fibers with smaller diameter; since the size of the surface regions is comparable to the overall fiber diameter.
CONCLUSION

Liner low density polyethylene fibers (LLDPE) with different solution concentration are adopted for electrospinning evaluation. The average fiber diameter gradually increases with the increasing of solution concentration. In addition, the increased concentration results fibers with higher crystallinity. From the WAXD analysis, it is determined that the crystallite size slightly decreased with crystallinity increasing. It is demonstrated by FTIR analysis that the high temperature electrospinning process does not change the chemical structure in the electrospun fibers.

The tensile tests with single fibers indicate the fibers with higher concentration exhibit better mechanical properties. And the mechanical properties of single fibers can be improved with incorporation of graphene. In addition, size effect is observed for both neat LLDPE and LLDPE/graphene composite fibers. That is at a certain concentration, both the modulus and strength values increased as the fiber diameter decreased and an abrupt change exhibits when fiber diameter is below 1μm.
REFERENCES

1. Formhals, A. U.S. Patent 1,975,504, 1934.


4. Ramakrishna, S.; Fujihara, K.; Teo, W.-E.; Lim, T. C.; Ma, Z. An Introduction to Electrospinning and Nanofibers; World Scientific: Singapore, 2005.


38. Berger C et al 2006 Science 312 1191


40. Coraux J, N’Diaye A T, Busse C and Michely T 2008 Nano Lett. 8 565


44. Li D, Muller M B, Gilje S, Kaner R B G 2008 Nature Nanotechnol. 3 101


61. Gogalewski S. Polymer 1977; 18: 63

62. Reneker DH, Chun I. Nanotechnology 1996; 7: 216

63. Doshi J, Reneker DH. J. Electrostat. 1995; 35: 151

64. Reneker DH, Yarin AL, Fong H, Koombhongse S. J Appl Phys 2000; 87(9 Pt 1):4531–47.


91. Reneker DH, Kataphinan W, Theron A, Zussman E, Yarin AL. Polymer 2002; 43: 6785


111. Huang ZM, Zhang YZ, Kotaki M, Ramakrishna S. Comp. Sci. Technol. 2003; 63: 2223


126. Chew SY, Hufnagel TC, Lim CT, Leong KW. Nanotechnology 2006;17: 3880–91